

PATENT SPECIFICATION

NO DRAWINGS

Inventor: BRION WELLER

L103,202



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Int. Cl.: —B 65 d 85/00

COMPLETE SPECIFICATION

ERRATA

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SPECIFICATION No. 1,103,202

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Page 2, line 58, after "solvent" insert "boiling"
Page 2, line 67, for "divide" read "divided"
Page 2, line 108, for "treatmen" read "treatment"
Page 3, lines 65 and 66, after "droplet" insert "or particle"

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THE PATENT OFFICE
18th March 1968

20 provided an encapsulated material which comprises droplets or particles of a solid or liquid first substance which is a hardening reagent for resins, a curing agent for natural or synthetic elastomers, or capable of reacting with one or more substances to produce an adhesive or surface coating composition, each

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agent being then dissolved in the dispersing medium to bring about the required reaction at the surfaces of the dispersed droplets. The encapsulated liquid can subsequently be allowed or caused to settle out, filtered off, washed and dried.

It is also possible to obtain the encapsulated

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Int. Cl.: —B 65 d 85/00

COMPLETE SPECIFICATION

Improvements relating to Encapsulated Materials

We, THE DUNLOP COMPANY LIMITED, formerly Dunlop Rubber Company Limited, a British Company of Dunlop House, Ryder Street, St. James's, London, S.W.1, formerly, 5 of 1, Albany Street, London, N.W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the 10 following statement: —

This invention relates to encapsulated materials, that is to say materials comprising droplets or particles of one substance each enclosed by a layer of another substance, the latter having the function of preventing the escape or reaction of the first substance until the enclosing layer is broken.

According to the present invention there is provided an encapsulated material which comprises droplets or particles of a solid or liquid first substance which is a hardening reagent for resins, a curing agent for natural or synthetic elastomers, or capable of reacting with one or more substances to produce an adhesive or surface coating composition, each droplet or particle being enclosed by a solid barrier layer, that is a solid layer which prevents escape or reaction of the said first substance until the layer is broken, the barrier layer being a product of the reaction of the said first substance with another substance. By the term 'surface coating composition' as used herein is meant a composition which when applied to a surface sets thereon to form a substantially uniform coating. Such an encapsulated material can be produced by taking droplets or particles of a first substance to be encapsulated and bringing about at their surface a chemical reaction between the said first substance and another substance 40

(referred to below as the "encapsulating reagent") that reacts with the first substance with the formation of a barrier layer over the surface of the first substance.

If the substance to be encapsulated is a solid, particles of it may suitably be stirred either into the encapsulating reagent itself, if it is a liquid, or into a solution of the encapsulating reagent in an indifferent solvent, stirring being continued long enough to form coherent continuous coatings over the particles, the coated particles being then washed and dried.

If the substance to be encapsulated is a liquid, it may suitably be first dispersed, by stirring or other means, in a liquid which does not dissolve it but which does dissolve the encapsulating reagent, the encapsulating reagent being then dissolved in the dispersing medium to bring about the required reaction at the surfaces of the dispersed droplets. The encapsulated liquid can subsequently be allowed or caused to settle out, filtered off, washed and dried.

It is also possible to obtain the encapsulated materials by utilising solid-gas and liquid-gas interfacial reactions, provided a gaseous chemical is available which is capable of reacting with the compound in question and thus serving as the encapsulating reagent.

The substances which may be encapsulated in accordance with the present invention may be solids, pure liquids, solutions or dispersions, may be of organic and/or inorganic nature, and include for example polyepoxide resins, unsaturated polyester resins, phenol-formaldehyde resins, urea-formaldehyde resins, resorcinol-formaldehyde resins, melamine-formaldehyde resins, unsaturated hydrocarbon resins, diols, triols, and other polyols, poly-

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carboxylic acids, and polymerisable unsaturated monomers (e.g. ethylenic hydrocarbon monomers, acrylic monomers, and styrene and other vinyl monomers).

5 A system which depends for its operation on the mixing of two or more components shortly before use can be prepared well in advance if one or more of the components are encapsulated in accordance with the invention, the components being brought into intimate contact when required simply by the application of heat, pressure, or ultrasonic vibrations, for example.

10 The following are some instances of specific types of application of the technique of the present invention:

(1) Polyamines can be encapsulated by surface reaction with suitable polyisocyanates; the products form stable mixtures with poly-epoxide resins which can be caused to cure after rupture of the capsules by pressure (for adhesive applications) or by heating (for very rapid hot-curing uses).

(2) Conversely, polyisocyanates can be encapsulated by reaction with suitable polyamines. The product enables the preparation of stable mixtures which may be used to form polyurethane foams or polyurethane coatings (depending on the formulation) once the capsules have been ruptured.

(3) Labile liquid complexes of boron trifluoride can be encapsulated by surface reaction with solutions of an epoxide resin or styrene. In this form they give stable mixtures with polyepoxide resins, but cause rapid curing of the resins on rupture.

(4) Capsules of labile boron trifluoride complexes can be prepared by liquid-gas interaction. Droplets of the labile complex can be formed by means of an airless spray gun (i.e. one designed to atomise a liquid using the liquid pressure alone), or by means of a spray gun using an inert gas to form the spray, and can then be allowed to contact a gaseous olefine oxide, which will polymerise to form coatings over the droplets. Conversely, droplets of a polyepoxide resin an olefine oxide or styrene can be coated by surface polymerisation on contact with gaseous boron trifluoride.

55 The following Examples, in which the "parts" given are parts by weight, illustrate the invention:

EXAMPLE 1.

55 Encapsulation of a labile boron trifluoride complex.

60 In a glass vessel, 200 parts of a low-boiling petroleum naphtha hydrocarbon solvent at 70-95° C. and known as S.B.P.2 were stirred, using a stirrer giving high localized shear operating at approximately 3,000 r.p.m. To this stirred liquid were added 50 parts of a liquid consisting of 4 parts of a solvent bis-(tetrahydrofurfuryl) phthalate, and 1 part of boron trifluoride diethyl-etherate, followed by 3 parts of Aerosil 2491 (Trade Mark), a finely-divide silica. Stirring was continued at approximately 3,000 r.p.m. for 10 minutes, after which time the boron trifluoride complex, containing the Aerosil, was in the form of small droplets which settled to the bottom of the vessel but did not agglomerate.

65 A different stirrer was then used which gave much lower localised shear and greater bulk movement than that used previously. This stirrer was used at the minimum speed required to keep the droplets of the boron trifluoride complex suspended, and then 15 parts of vinyl cyclo-hexane diepoxide were added to the suspension. Stirring was continued for ten minutes, after which time the droplets (now coated) were separated from the suspending solution, were washed with more S.B.P.2 and were dried in air at room temperature.

70 The product was a dry powder which was graded into different particle sizes by sieving. The rough sieve analysis was as follows:—

| | | |
|------------------------|---------|----|
| Mesh size: 30 40 60 80 | pass 80 | 90 |
| Retained: 25 37 16 13 | 9 | 95 |

75 Samples of all these grades were gently mixed with ten times their weight of a bifunctional epoxide resin based on Bisphenol A and epichlorhydrin (known as Epikote 828 (Trade Mark)); the mixtures showed no sign of curing after two weeks. However, when films of these mixtures were subjected to pressure (between metal plates), the capsules ruptured and hardening of the resin system occurred within 4 minutes. Rupture of the capsules and subsequent curing of the resin system was also brought about by heating the mixture at 120° C for a few minutes.

80 The product was a dry powder which was graded into different particle sizes by sieving. The rough sieve analysis was as follows:—

| | | |
|------------------------|---------|----|
| Mesh size: 30 40 60 80 | pass 80 | 90 |
| Retained: 25 37 16 13 | 9 | 95 |

85 Samples of all these grades were gently mixed with ten times their weight of a bifunctional epoxide resin based on Bisphenol A and epichlorhydrin (known as Epikote 828 (Trade Mark)); the mixtures showed no sign of curing after two weeks. However, when films of these mixtures were subjected to pressure (between metal plates), the capsules ruptured and hardening of the resin system occurred within 4 minutes. Rupture of the capsules and subsequent curing of the resin system was also brought about by heating the mixture at 120° C for a few minutes.

90 Other samples of the capsules were immersed in toluene and in methyl ethyl ketone for six weeks, but were still capable of curing epoxide resins after this treatment. As both of these solvents rapidly dissolve the boron trifluoride complex in normal situations, it appears that they are incapable of passing through the coating of the capsules.

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EXAMPLE 2.

Encapsulation of an epoxide resin.

The method used corresponded exactly with that described in Example 1.

50 parts of the epoxide resin Epikote 828 and 4 parts of Aerosil 2491 were added successively to 200 parts of S.B.P.2 whilst the latter was stirred rapidly. After 10 minutes a suitable dispersion was obtained. Using the second stirrer mentioned in Example 1, the droplets were kept in suspension, and 6 parts of boron trifluoride diethyl-etherate were added. After 10 minutes, the particles were separated from the suspending solution, were washed with more S.B.P.2, and were allowed

to dry at room temperature in air. The product was not sieved.

5 A paste made from 3 parts of these capsules and 2 parts of a liquid consisting of 5 parts of boron trifluoride diethyl-etherate dissolved in 95 parts of bis-(tetrahydrofurfuryl) phthalate, was stable until the capsules were ruptured by pressure and shearing forces applied to the mixture. After rupture had been effected, the mixture became very hard within 5 minutes.

10 A powder consisting of 2 parts of these capsules and 1 part of the 40-mesh grade capsules described in Example 1 was squeezed between metal plates by a pressure of 100 p.s.i. It was found that a fairly homogeneous, hard film resulted after 3-4 minutes, bonding the metal plates together strongly.

EXAMPLE 3.

20 Encapsulation of an aliphatic polyamine. The method used corresponded with that of the previous examples.

25 40 parts of diethylene triamine and 5 parts of Aerosil 2491 were stirred into 200 parts of S.B.P.2. After a satisfactory dispersion had been obtained, the stirrer was replaced by the other stirrer mentioned in Examples 1 and 2. With this operating at the minimum speed required to maintain the droplets in suspension, 5 parts of tolylene 2,4-diisocyanate were added slowly. The droplets quickly received a coating by interfacial reaction, and were then removed from the system, were washed with S.B.P.2, and were dried in air at room temperature.

30 The product was a powder which had the following sieve analysis.

Mesh size: 30 40 60 80 pass 80
%:

40 Retained: 29 25 24 14 8

45 A sample of the second grade of these capsules was gently mixed with seven times its weight of Epikote 828. In this form the mixture was stable for several days; after subjection to vigorous shearing and squeezing actions designed to rupture the capsules, the mixture became warm and solidified after approximately 25 minutes.

50 The three types of capsules described in these Examples are all of use in the field of adhesives, and can also be used in the fields of surface coatings and the potting of electrical components. The capsules described in Example 3 can further be used in the curing of neoprene elastomers and like materials.

WHAT WE CLAIM IS:—

60 1. An encapsulated material which comprises droplets or particles of a solid or liquid first substance which is a hardening reagent for resins, a curing agent for natural or synthetic elastomers, or which is capable of reacting with one or more substances to

produce an adhesive or surface coating composition (as hereinbefore defined), each droplet being enclosed by a solid barrier layer, that is a solid layer which prevents escape or reaction of the said first substance until the layer is broken, the barrier layer being a product of the reaction of the said first substance with another substance. 65 70

2. A material according to Claim 1, comprising droplets of a polyamine enclosed by a barrier layer of a product of the reaction of the polyamine with a polyisocyanate. 75

3. A material according to Claim 1, comprising droplets or particles of a polyisocyanate enclosed by a barrier layer of a product of the reaction of the polyisocyanate with a polyamine. 80

4. A material according to Claim 1, comprising droplets of a liquid boron trifluoride complex enclosed by a barrier layer of a product of the reaction of a boron trifluoride with an epoxide resin or styrene or an olefine oxide. 85

5. A material according to Claim 1, comprising droplets of an epoxide resin, an olefine oxide or styrene enclosed by a barrier layer of a product of the reaction of boron trifluoride with an epoxide resin, and olefine oxide or styrene. 90

6. A method of producing an encapsulated material according to Claim 1, which comprises the steps of taking droplets or particles of a first substance to be encapsulated and bringing about at their surface a chemical reaction between the said first substance and another substance that reacts with the first substance with the formation of a barrier layer over the surface of the first substance. 95 100

7. A method according to Claim 6, in which the substance to be encapsulated is a solid and particles of it are stirred either into the encapsulating reagent (as hereinbefore defined) itself, if it is a liquid, or into a solution of it in an indifferent solvent, stirring being continued long enough to form coherent continuous coatings over the particles, the coated particles being then washed and dried. 105 110

8. A method according to claim 6, in which the substance to be encapsulated is a liquid, and it is first dispersed in a liquid which does not dissolve it but which does dissolve the encapsulating reagent, the encapsulating reagent being then dissolved in the dispersing medium to bring about the required reaction at the surfaces of the dispersed droplets. 115 120

9. A method of making an encapsulated material, substantially as described in any of the Examples given above.

10. An encapsulated material made by a method according to any of claims 6 to 9. 125

11. An adhesive or surface coating composition (as hereinbefore defined) comprising two or more components in which at least

one component is an encapsulated material according to any one of Claims 1 to 5 or 10 and at least one component is a substance capable of reaction with the encapsulated material.

5 12. A method of making an adhesive or surface coating composition (as hereinbefore defined) which comprises mixing together two or more components at least one of which 10 is an encapsulated material according to any

one of Claims 1 to 5 or 10, and at least one of which is a substance capable of reaction with the encapsulated material.

13. An adhesive or surface coating composition (as hereinbefore defined) when made 15 by the method of Claim 12.

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